HIDES PRESERVED WITH LOW LEVELS OF SO_2. THE EFFECT OF REDUCED TEMPERATURES AND ADDED SALTS ON EXTENDING PRESERVATION*

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Abstract

Reducing the odor of SO_2 is important in its use, since it is a toxic and irritating gas. Hide samples that were treated with 0.33 percent SO_2 were preserved for up to 5 days at 30°C with little or no odor of SO_2 after treatment or storage. The applicability of this method has been further enhanced by methods which increase the preservation time. If samples treated with this concentration of SO_2 were given a flesh surface treatment of (1) 10 percent NaCl or, (2) 1 to 2 percent $NaHSO_4$ and stored at 30°C or, (3) just stored at 4°C with no post treatment, the preservation time could be extended to at least 28 days. In addition, hide samples could be treated by soaking for 6 hr in acid solutions of sulfite salts that had little or no odor of SO_2. The preservation time of these samples could be extended from approximately 3 days at 30°C to at least 28 days when stored at 4°C. The simplest method of extending the preservation time of hide samples treated with 0.33 percent SO_2, storage at 4°C, was tested on a larger scale. Full hides so treated were satisfactorily preserved for 5 weeks and the preserved hides were processed commercially into acceptable leather. The concepts that were used and their applications to the preservation of hides in general are discussed.

Introduction

Our laboratory has studied and reported on the use of gaseous SO_2 to preserve hides (1). Cowhides that were treated with 1.32 percent SO_2 were preserved for 1 month as determined by the control of microbial numbers, observation, and the commercial acceptability of the leather produced from the preserved hides. Acidification of hides before treatment with SO_2 significantly lowered the amount of SO_2 needed for short or extended-term preservation. The effect of the concentration of SO_2 on the duration of preservation and the odor of SO_2 after treatment and storage was evaluated. Small-scale studies showed that when slight excesses

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of SO_2 were used, as defined by odor after a 20-hr treatment, this excess could be removed by flushing the treatment vessel with air. This procedure did not affect the preservation characteristics as determined by microbial count, proteolytic activity, and comparison with the control samples. The advantages and disadvantages of the use of SO_2 gas as a hide preservative were discussed.

Additional studies were reported that evaluated the effects of length of time of exposure to various concentrations of SO_2 gas on the duration of preservation characteristics and the odor of SO_2 after treatment and storage. It was found that hide samples treated with lower levels of SO_2 (0.33 percent SO_2) were preserved up to 5 days at 30°C and the SO_2 odor was either fleeting or unnoticeable after treatment and storage. It was shown that hides exposed to 0.66 percent SO_2 for 3 hr were preserved satisfactorily for up to 2 weeks and were made into commercially acceptable leather. Small-scale experiments indicated that the SO_2 preservation had the potential for long-term storage of up to 4 months. The importance of storing SO_2 preserved hides in containers that did not lose SO_2 and that were inert to hydrated SO_2 was demonstrated. Factors that can be important to maximize storage time and reduce the chances of damage to the leather-making properties of the hide were discussed (2).

This report is a continuation of our work on the use of SO_2 as a hide preservative with emphasis on limiting the amount of SO_2 used in order to control residual SO_2 odor. Since SO_2 is a toxic gas, the control of amount used and thus avoidance of excess is an important aspect in its application. From our previous studies, we have shown that the SO_2 odor was fleeting or unnoticeable after treatment and storage if low levels of SO_2 were used. The usefulness of this approach was limited, however, because of the short duration of preservation (approximately 3 days on hides stored at 70°F). If the storage time could be extended to 28 days, the value and applicability of this treatment would be greatly increased.

The treatment of hides with low levels of SO_2 will temporarily reduce microbial numbers and proteolytic enzyme activity. Storage of these SO_2-sanitized hides at low temperature should also help maintain the desirable effects of reduced microbial numbers and enhance the storage life of this product.

This study will report on the effects of storage at controlled low temperatures on extending the preservation time of hide samples sanitized with low levels of SO_2. In addition, we shall report on the effects of the following additional methods on extending the preservation time of such hides: 1) treatment of the flesh surface with 5 or 10 percent NaCl and 2) lowering the pH with a flesh surface treatment of 1 or 2 percent $NaHSO_4$.

Materials and Methods

For small-scale work, samples were cut from fresh, frozen hide pieces. Large-scale experiments were carried out on cowhides obtained immediately after slaughter and treated within 3 to 4 hr. The source of sulfur dioxide used for

treating the small-scale samples of hides was $NaHSO_3$ (Baker Analyzed Reagent*). When hides were treated, gaseous sulfur dioxide was added from a lecture bottle.

$NaHSO_3$ contains 66.3 percent sulfur dioxide by assay. In the tables, and initially in the text, the concentrations of $NaHSO_3$ used as a source of sulfur dioxide is followed by a figure in parenthesis which refers to the theoretical amount of sulfur dioxide available, e.g., 1 percent $NaHSO_3$ (0.66 percent SO_2), 0.5 percent $NaHSO_3$ (0.33 percent SO_2), etc. The weight of $NaHSO_3$ used was based on the weight of the sample to be treated.

LABORATORY STUDIES. Plastic racks were constructed to fit into desiccators (250 MM I.D.) and the samples of hide to be treated were draped over these racks. An acid stock solution was prepared to contain 1 volume of concentrated sulfuric acid per 2 volumes of water. A 50-ml Erlenmeyer containing 2 ml of this acid solution per gram of $NaHSO_3$ to be used was placed with desiccator. The SO_2 was generated by adding the $NaHSO_3$ to the Erlenmeyer. The desiccator was then sealed and left to stand at ambient temperatures overnight.

Those SO_2-treated samples that were to be stored at 12°C and 4°C were transferred to mason jars, sealed, and then placed in the controlled temperature rooms. The SO_2-treated samples that were to be treated with NaCl or $NaHSO_4$ were placed hair side down on a plastic sheet. These samples were then treated by sprinkling either 5 or 10 percent NaCl, or 1 or 2 percent $NaHSO_4$, as evenly as possible over the flesh surface. The samples were folded, placed on plastic racks contained in a plastic box, sealed, and allowed to drain approximately 24 hr. They were then carefully transferred to mason jars and stored at 30°C. In all cases, a double thickness of Saran wrap was placed between the lid liners and jars to prevent any corrosion of the liner.

An additional experiment was carried out to test the effect of storage at 30°C and 4°C on samples that were soaked in acid sulfite solutions that were relatively free of SO_2 odor. The compositions of the solutions are shown in Table I. Concentrations of ingredients were based on the weight of the hide samples that were used. The samples were soaked for 6 hr, allowed to drain for 15 min, and transferred to mason jars for storage at 30°C and 4°C.

Large-Scale Study. A 4′ × 4′ × 8′ plywood box fitted with wheels and lined with urethane foam panels was used as a treatment chamber. The four fresh hides were hung hair side down over notched, wooden 2′ × 4′ supports (1). A lid was placed on the box and the edges were taped. The SO_2 was added from a lecture bottle through Tygon tubing which led to a trap and then into the box. The amount of gas added was determined by weighing the cylinder before, during, and after gas addition. An exit tube led from the box to a bubbler containing water to detect and allow any excess pressure to escape. It took about 30 min to

TABLE I

EFFECT OF 6-HR SOAK IN ACID–SULFITE SOLUTION
SAMPLES DRAINED FOR 15 MIN AND STORED AT 4°C*

Float, HAc, Na_2SO_3 (%)	Before Soak pH	After Soak pH	Bact. Wash pH	Bact./g Hide
			After 32 Days Storage	
100, 1, 1	4.5	4.7	5.1	7,000
200, 1, 1	4.5	4.8	5.3	17,000
100, 1, 1.5	4.8	5.2	5.4	3,000
100, 1, 2	5.1	5.3	5.4	11,000
			After 48 Days Storage	
100, 0, 2**	4.2	5.6	5.6	140,000

*1-hr GFA = 0 on all samples.
**$NaHSO_3$ used alone in place of HAc and Na_2SO_3.

add the gas. The cylinder must be warmed by immersing in warm water (not to exceed 125°F) to overcome the cooling effect of the expanding gas. There was no evidence of pressure buildup in the treatment chamber as indicated by gas bubbling through the water in the exit trap in any of our large-scale tests.

After the designated exposure time, the lid was partially removed and then totally removed to allow the excess gas to dissipate. (This latter procedure should be done out-doors and with adequate ventilation because sulfur dioxide is a toxic and irritating gas.) The hides were transferred manually to individual Fiberglas boxes which were sealed with tape at the juncture of the lid and box. Two boxes were stored at room temperature (21°C) and two were stored at 4°C. Before the hides were taken to the tannery for processing, samples were cut from the edges, and transferred to weighed mason jars. These samples were used for the 1-hr gelatin film tests and microbial counts. At the tannery, the hides were split into sides before processing into side leather.

Analytical Methodology. For determinations of microbial counts, 500 ml of sterile water was added to the sample which was then shaken for 15 min on a reciprocating shaker at approximately 200 rpm. The standard plate count was carried out with serial dilutions from the wash solutions. Samples from each dilution were plated in duplicate on standard plate count agar. The plates were counted after incubation for 72 hr at 30°C.

The solution used for bacterial counts (referred to as the bacterial wash solution) was measured for pH. If a sample showed no obvious signs of deterioration, such as odor or visible growth, a 1-hr gelatin film activity was run to test for proteolytic enzyme activity. This test will be referred to as the 1-hr GFA in the text. The method was developed by Rolf R. Schmitt and Clara Deasy (3, 4).

The experimental sides of leather (garment/light-shoe-upper leather) were tested for tensile strength (5) and SATRA grain crack (6, 7). This latter test followed the methods of the International Union of Leather Chemists' Societies,

where it is called the "Ball Burst Test." A SATRA extension at grain crack of 7 mm or more should give a leather satisfactory for lasting in most cases. A result less than 6 mm indicates that the leather is unsuitable for lasting. The leathers were also given a subjective quality evaluation by the commercial tanner who processed the experimental hides.

It is important to note that the pH of the SO_2 treated hides will need to be raised before processing. If sulfides are added to the unhairing solution before the pH is raised with lime, the evolution of toxic hydrogen sulfide could occur. Therefore, it is essential that this precaution be observed.

Results

The Effects of Reduced Temperatures. Our past studies have shown that hide samples that were exposed overnight (20 hr) to the SO_2 evolved from 0.5 percent $NaHSO_3$ (0.33 percent SO_2) and stored at 30°C were preserved up to 5 days with control of microbial numbers and proteolytic enzymes. Untreated samples showed no control of microbial growth and proteolytic enzyme activity was detectable after 3 days. Samples treated as described above and controls were stored at 4°C and 12°C. Figure 1 is a graphic representation of the microbial counts obtained from these samples plotted against time. The appearance of visible growth or a positive 1-hr GFA is also noted.

Treated samples stored at 12°C maintained low microbial numbers and con-

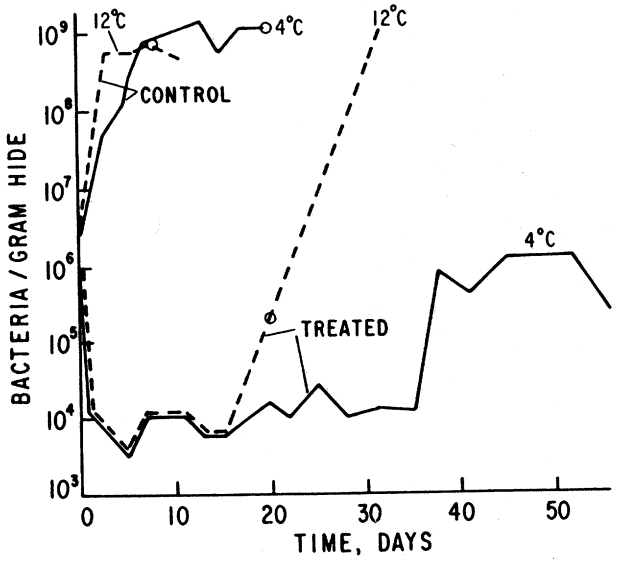

FIGURE 1. — Effect of storage of SO_2 treated hide samples at 12°C or 4°C. SO_2 source 0.5 percent $NaHSO_3$ (0.33 percent SO_2). O on curve equals time at which visible growth occurred or a positive 1-hr GFA was obtained.

trol of proteolytic enzyme for 15 days which reflects a significant gain in preservation time when compared to a 5-day hold at 30°C. Treated samples stored at 4°C however, show a dramatic gain by extending preservation time up to 56 days.

The increase in preservation time at lower temperatures can be explained by a reduced rate of biochemical activity. Additionally, the rate of oxidation of SO_2 to SO_3 and the combination of SO_2 with other compounds is likely reduced. The solubility of SO_2 increases and the volatility decreases as the temperature is lowered. These factors tend to conserve SO_2 and to retain it in the hide. Since low concentrations of SO_2 were used, the conservation of SO_2 can be expected to be a critical variable.

The advantage gained in storage of the controls (untreated samples) at lower temperatures appears to be the inhibition of the appearance of proteolytic enzyme activity. Enzyme activity was detected after 3 days at 30°C, 7 days at 12°C, and after 20 days at 4°C. Microbial numbers are not lowered but the initial surge of growth as it proceeds to its upper limits is slowed somewhat. The lower the temperatures, the greater the relative inhibition as would be expected.

Storing the low level SO_2 sanitized hide samples at 4°C was so effective that it was of interest to test this approach on samples that were exposed for 1, 2, and 4 hr to the SO_2 evolved from 0.5 percent $NaHSO_3$. In past work, and repeated in this experiment, samples that were so treated and stored at 30°C gave a 3-day preservation (2). When stored at 4°C however, all samples, regardless of exposure time, were preserved for 32 days. No proteolytic activity was noted, the bacteria per gram of hide ranged from 22×10^3 to 37×10^3, and the bacterial wash pH's ranged from 5.2 to 5.3.

The next experiment tested the effects of an overnight exposure of hide samples to the SO_2 evolved from 0.4 percent $NaHSO_3$, 20 percent less than had been used in previous experiments. Fleshed and unfleshed samples were treated and stored at 30°C and 4°C. Samples were preserved up to 3 days at 30°C but, after 5 days, growth was visible on both fleshed and unfleshed samples. The results in Figure 2 show that storage at 4°C resulted in control of microbial numbers for 31 days with no detectable proteolytic enzyme activity.

Control of SO_2 Odor of Solutions and Effects of Low-Temperature Storage. Control of the odor of SO_2 is also important to the acid sulfite preservation systems that, in past work, we have applied to the hides in a solution (8-10). The acid sulfite solutions used for this study had relatively little odor of acetic acid or SO_2. Table I describes the solutions used and shows that the samples which had been soaked for 6 hr and then stored at 4°C were preserved for at least 32 days. All the samples stored at 30°C had failed after 6 days except those soaked in a 2 percent $NaHSO_3$ solution. These latter samples maintained microbial numbers at about 600×10^3 bacteria per gram of hide for 6, 11, and 13 days, but after 15 days, counts increased to 11×10^6 indicating that microbial control was beginning to fail. These samples, when stored at 4°C, were still preserved after 48 days.

The odor of SO_2 was controlled in these soak treatments by the use of rela-

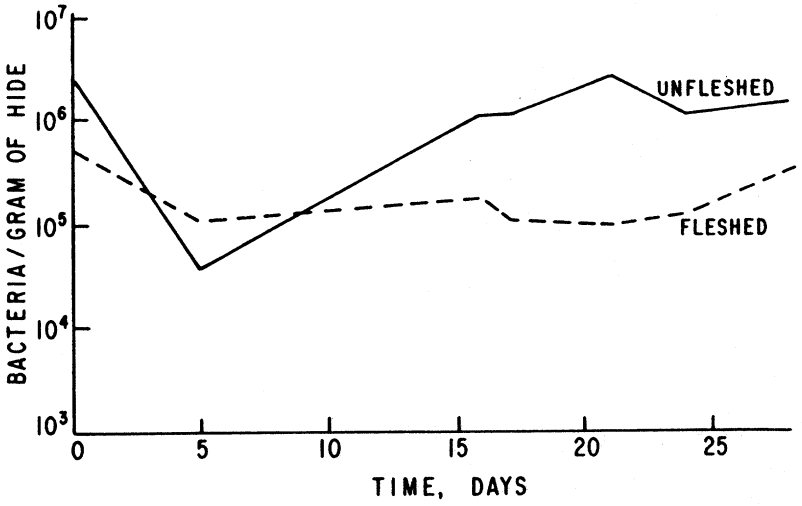

FIGURE 2. — Effect of storage of SO_2 treated hide samples at 4°C. SO_2 source 0.4% $NaHSO_3$ (0.25 percent SO_2).

tively dilute solutions of preservatives and by pH. For example, in the distribution H_2SO_3, HSO_3^-, and $SO_3^=$, as the pH rises from 4.0 to 4.97; the relative concentration of H_2SO_3 goes from 0.60 to 0.04 percent (11). Since the SO_2 odor arises from H_2SO_3 ($H_2O.SO_2$), the SO_2 odor is also reduced. The preservation effectiveness, however, would tend to decline because H_2SO_3 is significantly more effective than HSO_3^- as a microbial preservative (12). This decrease of effectiveness was likely countered by the effects of low-temperatures storage at 4°C.

The Effects of Added NaCl. The next experiments on extending the preservation time of SO_2-sanitized hide samples examined the effect of treating the flesh side of the samples with 5 or 10 percent NaCl as described in Materials and Methods. The samples were held at 30°C. Table II shows that hide samples that received (1) no treatment spoiled in 3 days; (2) 5 or 10 percent NaCl only spoiled in 4 days; (3) just SO_2 treatment were preserved for 5 days; and (4) SO_2 treatment plus 10 percent NaCl were preserved for at least 28 days, the duration of this experiment.

There was some inhibition of microbial growth when hide samples were treated with NaCl alone. A 5 or 10 percent NaCl treatment gave counts of 173×10^6 and 71×10^6 bacteria per gram of hide, respectively, after 4 days. Without NaCl, the count would be in the billions after this time. The critical test for hide spoilage in this case was the 1-hr GFA which detected proteolytic enzyme activity which correlates with grain damage (3,4).

TABLE II

HIDE SAMPLES EXPOSED TO THE SO_2 EVOLVED FROM 0.5 % $NaHSO_3$ (0.33% SO_2) FOR 20 HR THEN TREATED WITH SOLID NaCl OR $NaHSO_4$ SPREAD OVER FLESH SURFACE (SAMPLES ALLOWED TO DRAIN 24 HR, THEN STORED AT 30°C)

NaCl Treatment			Storage Time	$NaHSO_4$ Treatment		
NaCl %	Bact. Wash pH	Bact./g Hide × 10^3	Days	$NaHSO_4$ %	Bact. Wash pH	Bact./g Hide × 10^3
			Treated Samples[a]			
5	5.3	7,500	14	1	4.3	6
5	5.4	13	14	-	-	-
5	6.5	Vis. growth	28	1	4.0	6
5	4.6	19	28	-	-	-
10	5.1	8	14	2	3.5	5
10	5.0	5	14	-	-	-
10	4.9	57	28	2	3.2	2
10	4.6	17	28	-	-	-
			Controls (No SO_2 pretreatment)[b]			
0	-	Spoiled	3	-	-	-
5	-	173,000	4	1	-	Vis. growth
10	-	71,000	4	2	-	Vis. growth

[a] Samples treated with SO_2 alone maintained control of bacteria and proteolytic enzymes for 5 days. 1-hr GFA = 0 on all samples without visible growth.

[b] 1-hr GFA = 3 on all NaCl controls.

The variable results that were obtained with a 5 percent NaCl treatment of the SO_2 treated samples and the success obtained with a 10 percent treatment indicated that a 5 percent NaCl treatment was at the lower limits of effectiveness using this technique. It does have some effect, however, since it did extend the preservation from 5 days up to 14.

The average weight loss and the estimated amount of NaCl retained by the hide samples treated with NaCl were as follows: 5 percent NaCl, 4.6 percent weight loss, 3.4 percent NaCl retained; 10 percent NaCl, 9.4 percent weight loss, 6.5 percent NaCl retained. Assuming that the weight loss is mainly water (dehydration) and that the NaCl retained by the hide increases the osmotic pressure in the remaining hide moisture, we have two effects that will act to inhibit biological and chemical activity. These effects of the NaCl plus the SO_2 in the sample result in the synergistic effect that was observed in this preservation. The ability of the SO_2 treatment to lower microbial numbers and control biological activity until the NaCl can equilibrate in the hide components is a likely reason for the effectiveness of this preservation approach since Cooper *et al.* have reported that the period of delayed cure can last for 6 to 12 hr after stack salting (13).

The Effects of Added $NaHSO_4$. The amount of SO_2 evolved from 0.5 percent $NaHSO_3$ (0.33 percent SO_2) and absorbed by the hide sample over a 20-hr

period has been shown to be sufficient to give a preservation time of at least 28 days at 30°C if the hide sample was acidified before the SO_2 treatment (1). The lowering of the pH by the $NaHSO_4$ is mainly responsible for the increase in preservation time, since it increases the concentration of undissociated H_2SO_3 (12). Table II lists the results that were obtained when hide samples were acidified after the above SO_2 treatment by sprinkling 1 or 2 percent $NaHSO_4$ over the flesh surface. The samples were allowed to drain for 24 hr in a closed container but relatively little drainage was observed. The results show that this treatment can be used to extend the preservation time of hide samples treated with low levels of SO_2 from 5 to at least 28 days with effective control of microbial numbers and proteolytic enzyme activity.

Large-Scale Tests. Two cowhides were treated with 0.33 percent SO_2 and stored in fiberglass boxes at approximately 21°C for 3 days. Based on evidence from small-scale studies, this treatment was proposed as a potential 2 to 3-day preservation with the control of SO_2 odor that could be practical to some users (1). This experiment was set up to corroborate these results on full hides.

In addition, two cowhides were treated with 0.33 percent SO_2 and stored in fiberglass boxes at 4°C. One was stored for 4 weeks and the other for 5 weeks. Of the methods tested on hide samples to extend preservation, this treatment was chosen for large-scale tests since it was the simplest and no further additives were needed. Large-scale controls were not set up at 4°C since small-scale results showed that microbial growth under these conditions was only slowed down and soon reached counts of a billion per gram of hide. (Also, these hides would have to be hung and exposed to circulating cold air to approach the results obtained on small samples.)

Table III shows that all of the conditions tested resulted in a reduction and control of microbial numbers as well as control of proteolytic enzyme activity during the storage periods tested. The SO_2 odor after treatment or storage was judged as negligible or unnoticeable. The physical tests data on the leather prepared from these preserved hides showed that the SATRA extensions were all above 7.0 mm which indicated good lasting properties. The tensile values were in an acceptable range for the leather made from hides stored at 4°C but were low for those stored at room temperature. The tanner judged all the leather to be of commercial quality.

A variable that was not controlled in this experiment was found later to be that hydrated SO_2 did attack the interior of these fiberglass storage containers, particularly the lid. This effect could have contributed to the lower tensile values observed with hides stored at room temperature. The preserved hides stored directly in these boxes and held at 4°C did not show any deleterious effects however. This could be explained by the effects of the lower temperature which reduces chemical activity and increases the solubility and reduces the volatility of SO_2 in the hide components. This favors retention of the SO_2 by the hide.

TABLE III

MICROBIAL COUNTS ON HIDES TREATED WITH 0.33% SO_2 PHYSICAL TEST DATA ON LEATHER

Storage		Bact. Wash			Tensile[b]		SATRA
Time (Days)	Temp. (°C)	pH	Bact./g Hide	Side[a]	Elong. (%)	Ten. (PSI)	Ext. (mm)
3	21	4.5	30,000	L	35.13	1112	8.46
				R	30.25	1057	8.78
3	21	4.3	140,000	L	33.75	1354	8.59
				R	29.88	1124	7.36
28	4	4.4	18,000	L	42.33	2420	8.65
				R	41.75	2443	8.30
35	4	4.7	77,000	L	35.33	2392	8.51
				R	34.80	2196	8.81

1-hr GFA = 0 on All Samples

[a] Before processing at tannery, hides were split into sides.
[b] Average of three values ran parallel to backbone.

Regardless of the favorable outcome at 4°C, it is recommended that the hides be stored in containers that are inert to and do not lose SO_2.

Discussion

The Importance of Low Temperature in Hide Preservation. Temperature control as an adjunct to hide preservation becomes apparent when one considers that chemical reaction rates are generally halved or doubled and biological reaction rates can change by a factor of 4 to 7 times for every 10°C change. Enzyme activity and mean generation time of bacteria usually functions within a temperature range above or below which activity ceases or changes precipitously, e.g., as you approach freezing at 0°C or the denaturation temperature at 60°C. Many bacteria (Mesophiles) multiply rapidly between 70°F to 100°F and, under ideal growth conditions, can double every 20 min (1 bacterium increasing to 2×10^6 within 7 hr) (14).

Low temperature, in particular, has a significant effect in controlling the quality of hides which have already been treated with preserving agents. Mr. Hrones of Swift & Company stated that decomposition of properly cured (salt) stock is normally not a problem so long as contamination is avoided and low-temperature conditions are maintained. In the absence of low temperature control, particularly for extended storage or shipping, trouble is assured (15). Cooper has reported that leather from hides stored at 10°C, whether salted or treated with a biocide, were stronger than leather from hides stored at 25°C (16).

In this study factors that contributed to the synergistic effect that was noted between low temperature and SO_2 which gave significant increases in the storage

time of hides have been previously mentioned. The net result was a reduction and control of microbial numbers and proteolytic enzyme activity until the hide itself could equilibrate to the low storage temperature of 4°C. This effect was a critical goal in our work on hide preservation which was to conserve and upgrade that portion of the hide not used for leathermaking for byproduct uses. Storage of an untreated hide at low temperatures may preserve the leathermaking properties but the high microbial numbers that develop would have a detrimental effect on the suitability of byproducts for human and animal uses.

Hides sanitized with low levels of SO_2 (and likely other biocides or biostats) before storage at low temperatures have an additional property that deserves further study. Their significantly reduced microbial numbers and residual effects of the preservative used inherently gives more time, possibly 24 to 48 hr, before such hides would have to be processed after removal of low temperature controls. Such a sanitizing effect can be accomplished in a simple wash or soak as has been demonstrated in this study. Biological activity on unsanitized hides stored at 4°C however, would begin to accelerate as soon as the temperature began to rise. Since our data has shown that the microbial counts approaches 1×10^9 per gram of hide after 7 days at 4°C, such hides would need to be processed as soon as low temperature controls are removed. In fact, Lhuede and Scroggie suggest that even hides that have been frozen would have to be thawed in less than 24 hr as longer could result in damage to the hide (17).

Modifications of the SO_2 Low Temperature Method. Hides can be cooled while suspended in an insulated treatment container during the SO_2 application instead of cooling after treatment. The hide surfaces are exposed and would be cooled more efficiently. The lowered temperature reduces the volatility of SO_2 and increases its solubility in the hide components. (The weight percent water solubility of SO_2 at 1 atm is 10.14 at 20°C and 18.59 at 0°C.) These characteristics act as additional controls of SO_2 odor and probably effect a more rapid uptake of SO_2 by the hide. The chilled hides can now be stored in a cold room in much larger containers or packs than would be possible if they had not been chilled during treatment. Hides chilled to 4°C (or lower) during treatment could also be stored in an insulated container at ambient temperatures with the likelihood of an extended preservation, the time of which would depend on the external temperatures and the efficiency of the insulation of the container.

The Effects of Using NaCl with Other Preservatives. A concentration of salt much above 1 percent is reported to be harmful to many bacteria but not, of course, to halophiles. For the most part however, high concentrations of salt (10-15 percent) inhibit microorganisms (18). Paukner and Schmidt reported that when even the most potent biocides were tested on hide pieces, they did not preserve them for more than 2 weeks unless 3 to 5 percent was employed. The most economical way of extending curing times was to use 1 percent biocide in the presence of 5 or preferably 10 percent NaCl (19).

A recent paper by Russell and Galloway thoroughly covers the effects of low-

salt antiseptic curing of hides. They concluded that enhanced antiseptic activity occurs in the case of a number of commercial antiseptics when they are applied to hides in a dilute salt solution (20). Our results also indicate that enhanced antiseptic activity occurs when hide samples that were treated with low levels of SO_2 were given a flesh surface application of 10 percent NaCl. The data indicate that if hides were sanitized before a salt cure, the salt retained by the hide might need be less than 10 percent to obtain a cure of a month or possibly longer. Additional advantages of this approach, if appropriately designed, would be the prevention of protease activity in the hide and the elimination of the problems associated with delayed cure.

Although much more work needs to be done, the results of this study and the work done by others (19-21), indicates that short-term cures for hides can be extended in a variety of ways to increase their applicability and usefulness. The use of low-temperature storage as an adjunct to a preservation system for hides is important not only to supplement the control of microbes but to control enzymatic and chemical activity. Additionally, the use of a wider variety of preservatives at a lower concentration than would normally be used, should be possible if one is only sanitizing the hide rather than preserving it without the low-temperature assist.

Our results suggest that preservation systems that are marginal or inefficient at 30°C should be reevaluated at a lower temperature such as 4°C or with salt or both. Preservations that are effective should also be reevaluated in a similar fashion at much lower concentrations. It is apparent that various combinations of biological inhibitors can be incorporated into one preservation system to more effectively control the complex variables encountered in preserving a fresh hide. We have suggested and used this approach in our past work (8).

Summary and Conclusions

An advantage of preserving hide samples with low levels of SO_2 (0.33 percent) is that the SO_2 odor is negligible after the treatment. Under laboratory conditions, such samples are preserved up to 5 days at 30°C. Under commercial conditions using full hides, one might expect a 2 or 3-day preservation. In this study, we have demonstrated a number of ways to extend the preservation time of the treated hide samples which could increase the usefulness and applicability of this low-level SO_2 treatment.

One way is to store the treated samples at 12°C or 4°C which, in small-scale studies, extended the preservation to 15 and 56 days, respectively. Another way is to treat the flesh surface of the treated sample with 5 or 10 percent NaCl which resulted in a 14 and 28-day preservation, respectively at 30°C. A third way is to sprinkle the flesh surface of the treated samples with 1 or 2 percent $NaHSO_4$. This resulted in a 28-day preservation at 30°C.

The odor of SO_2 and acetic acid can also be a problem with acid sulfite

solutions. We have demonstrated in small-scale studies that such solutions can be prepared that have negligible odor. Samples that were treated by soaking in these solutions for 6 hr and stored at 4°C were preserved for at least 31 days. When stored at 30°C, all the samples were obviously spoiled after 6 days.

A large-scale test was carried out on full hides which were treated with 0.33 percent SO_2 and then stored at 30°C and 4°C. The odor of SO_2 was negligible after the treatment. Hides were satisfactorily preserved for 3 days at 30°C and for 4 and 5 weeks at 4°C and were processed into commercially acceptable leather. The results obtained at 4°C demonstrates the potential of this treatment to maintain control of microbes and proteolytic enzymes until the hides, which were stored in boxes, could equilibrate to the temperature of the cooler. Without this pretreatment, the insulating properties of the hide stored in the box would retard heat loss from the interior of the hide and this could result in localized damage to the hide. Although low temperature alone can be used to preserve the leather making quality of hides, they should be sanitized first to reflect commonly accepted practices of good housekeeping which contributes to shelf life. Appropriately done, it can protect health and conserve the value inherent in the hide for human and animal end use.

The preservation methods which have been reported on by this laboratory are meant to compliment, support, and encourage the use of fresh hides, the optimum substrate.

The preservation described in this study will result in a product which we have termed "fresh type" hide which has been defined in previous publications and presentations (1, 22). Our purpose was to try and preserve the total value inherent in a hide which we view as the first and most important step in hide processing. In support of this, consider the following advantages that can be gained if a fresh hide is appropriately preserved: 1) the elimination of the high-dissolved solids and Na ion pollution resulting from salt curing; 2) the potential for recovery of the 2/3 of the hide not used for leather making for known and valuable end product uses and a concomittant reduction in solid and process pollutants; and 3) the ability to be processed with or like fresh hides with no major changes in processing and the savings of water, energy, and time that result from fresh hide use.

This latter property allows a processor to schedule production based on fresh and/or "fresh type" hides. These factors should provide sufficient incentive to support the effort needed to begin to evaluate appropriate methods, based on the concepts in this and past papers from this laboratory or others, on a scale that can provide the hard operating and economic data necessary to move from bench to practice. This can provide the necessary feedback to design and develop appropriate equipment, storage systems, and better methods to allow the U.S. hide industry to recover the full economic value present in a hide.

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